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DETERMINATION OF THE SIZE OF SUBMICROSCOPIC PARTICLES BY X-RAYS

BY A. GUINIER

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TRANSLATED FROM THE JOUR.
CHIM. PHYS., 40, 133, 1943
BY

RUTH F. BRINKLEY AND STUART R. BRINKLEY, JR.

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DETERMINATION OF THE SIZE OF SUBMICROSCOPIC PARTICLES BY X-RAYS[1]

By A. Guinier[2]

Translated from the Jour. Chim. Phys., 40, 133, 1943

By Ruth F. Brinkley[3] and Stuart R. Brinkley, Jr.[3]

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INTRODUCTION

We know that when a beam of light passes through a medium containing small opaque grains, a halo of diffracted light is formed by the grains around the incident beam. As example, we may take the halo produced around the moon by droplets of mist and the well-known classroom experiment with powdered lycopodium. The intensity of the diffracted light is greatest in the direction of the incident rays themselves, decreases with the angle ε given approximately by the fundamental equation:

$$\varepsilon = \frac{\lambda}{d}, \qquad (1)$$

where λ is the wave length of the light and d the average diameter of the particles. For the phenomenon to be observable, the value of this diameter must be 10 to 100 times that of the wave length.

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This same phenomenon of diffraction may be transposed into the X-ray domain. All that is necessary is to reduce, in the same proportion, the wave length of the light and the diameter of the particle; thus, with radiations whose wave length is of the order of angstroms, the dimensions of the active particles go from 10 to 100 A - that is, the dimensions of colloidal particles. The evidence of this fact is shown by the following experimental scheme (fig. 1a): A narrow beam of X-rays passes through a thin layer of a medium containing micelles; the photographic film is placed a few centimeters behind the sample, and a small absorbing screen stops the direct beam in order to prevent its fogging the film. The intersect of the direct beam is surrounded by a narrow spot whose blackness decreases with the distance from the center. We will call this the spot of central diffusion (fig. 1b). The phenomenon, in spite of its relatively great intensity, has been observed only by a few authors,[4] who have simply given a qualitative description without attempting any quantitative deductions. This is due to the fact that observation of this phenonenon is not possible with the apparatus generally used to obtain X-ray diagrams, because the parasite foggings in the vicinity of the incident beam are sufficiently important to hide those produced by the sample. With the monochromator, however, used by us to obtain Debye-Sherer[5] diagrams, this parasitic diffusion can be totally suppressed. In this way our attention was again directed to the spot of central diffraction, and we were led to make a detailed qualtitative study of it. Since then several papers have been published on this subject. Hosemann,[6] using methods of calculation outlined by us, has extended them to the special case of fibrous substances. Kratky,[7] on the other hand, starts from an entirely different theoretical point of view; he examines the case, not of scattered particles, but of closely packed particles.

We will now describe the experimental methods, summarize the calculations needed in the elaboration of diagrams, and finally review the first results obtained in the vast domain of these new physical-chemical studies.

EXPERIMENTAL METHODS

Equation (1) shows that the greater the wave length, the greater the angle of diffraction, and therefore the more easily is it observed. Moreover, as the wave length increases, the X-ray absorption by the sample increases rapidly. It therefore becomes necessary to reduce the thickness of the preparation, that is, of the diffusing volume, thus increasing the exposure time. Therefore, one is greatly limited with respect to the long wave lengths. We have employed the CuK ($\lambda = 1.54$ A) currently used in crystal analysis. Hosemann used a somewhat greater wave length: the complex

4/ Raman, Nature, 124, 53 (1929); Warren, Phys. Rev., 49, 885 (1936.)
5/ Guinier, Ann. de Phys., 12, 161 (1939).
6/ Hosemann, Zeit, Physik., 113, 751 (1939); Ibid, 114, 133 (1939); Zeit. Elektro-Chemie, 46, 535 (1940).
7/ Kratky, Zeit. Elektro-Chemie, 48, 587 (1942).

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Plate 1

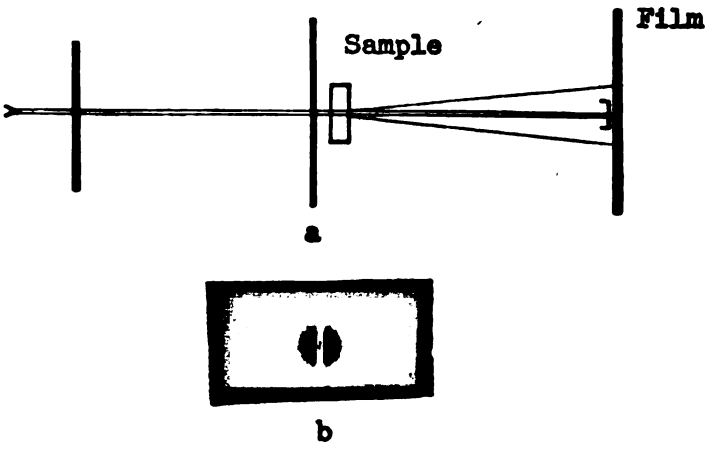

Figure 1

a) Diagram of the experiment.
b) Negative of central scattering for a sample of lampblack (actual size).

Distance from sample to film: 60 mm. CuK_α radiation.
Exposure: 1 hour.

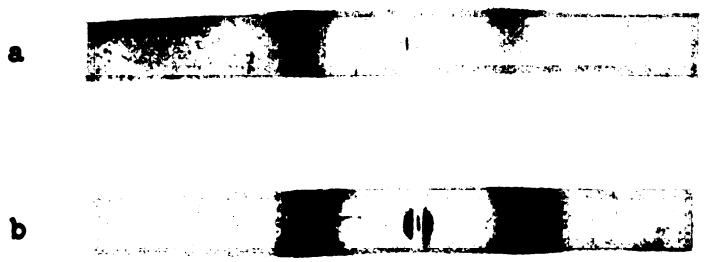

Figure 9

a) Pattern of solid plexiglass.
b) Pattern of an acetone solution of plexiglass.

Reproduced in full size. CuK_α radiation.
Distance from sample to film: 60 mm.

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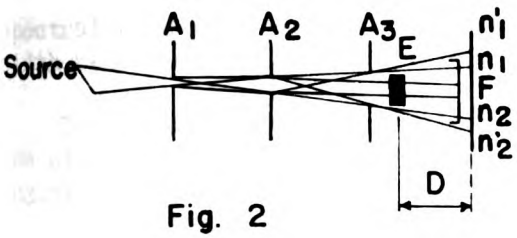

Fig. 2

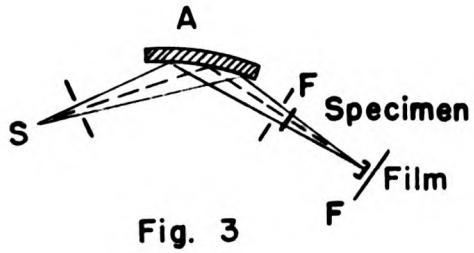

Fig. 3

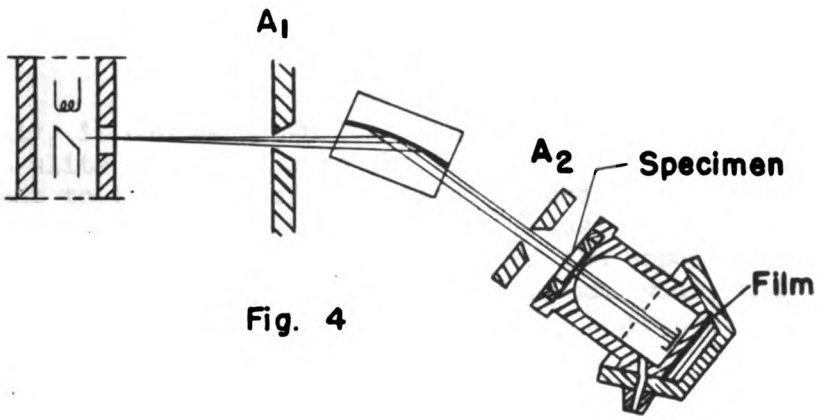

Fig. 4

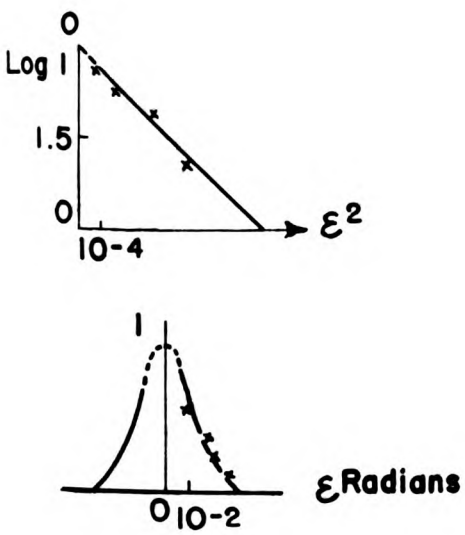

Fig. 5

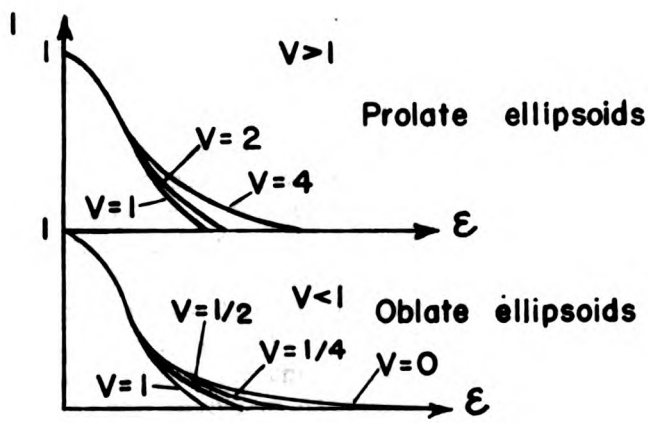

Fig. 6

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radiation produced by an aluminum anticathode in a low tension tube. The spectral band utilized has its center of gravity at about 3 Å, but its width reduces the accuracy of the measurement.

The essential condition that the experimental set-up must fulfill is the elimination of any parasitic fogging from even the smallest possible angle. The simplest arrangement is the following (fig. 2): two slits A_1 and A_2, determine a narrow beam of X-rays coming from a relatively wide source, S; the beam meets the sample, E, and covers the space, n_1n_2, on the film, F. On the other hand, the edges of the slit, A_2, touched by the X-rays emit secondary rays by diffraction or fluorescence. It therefore becomes necessary to protect the film from them by a third slit placed just in front of E and adjusted in such a way that its edges exactly limit the primary beam without touching it. Finally, it is only outside the interval, n_1n_2, that those beams alone, which are diffracted by the sample, reach the film. The minimum angle possible with this apparatus is

$$\alpha = \frac{1}{2}\frac{n_1n_2}{D}.$$

Geometrically, it can be shown that there exists an optimum position of the different slits in relation to the film, and that the minimum angle α is proportional to the width of the slits, A_1 and A_2, and inversely proportional to their distance. It is therefore desirable to reduce the slits, thus decreasing the amount of radiation of the apparatus. Thus, in Hosemann's apparatus the slits were only 0.0025 mm. wide, and the diagrams obtained started at an angle of 9.7 min.; the exposures were very long, in the order of 60 to 800 hours.

The installation used by us has already been described; a brief summary will recall its characteristics. Instead of using the continuous radiation of the anticathode, a monochromatic ray is isolated by means of a crystal sheet, from which the beam is reflected. A correct definition of the wave length makes a more accurate interpretation of the diffraction pattern possible, but the principal advantage lies in the geometrical properties of the monochromator used (fig. 3); this monochromator is formed by a plate of quartz that has been cut and curved. Under these conditions, all rays of a given wave length emanating from a narrow source, S, placed at a suitable distance from the crystal, may be reflected from the plate having a proper orientation and be made to converge in a point, F, placed at a distance, AF = AS. The diffracting sample is placed in the reflected beam at E; the photographic film passes through F. No matter what the width of the beam, and consequently no matter what the energy it possesses, the width of the ray, F, remains the same, whereas in the set-up having no monochromator, the opening of the slits results in a widening of the path of the direct beam. The rays diffracted at any given point of the sample at a given angle converge at the same point on the film. In this way the relative value of the definition of the angular diffraction does not become less accurate when the angle decreases, as is the case in other set-ups. As the plate of the monochromator on which the direct beam falls diffracts the X-rays, it becomes necessary, in order to avoid a parasitic

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blackening on the film, to place a slit whose edges do not touch the beam just in front of the sample. It has been shown that the best position for the sample is in the middle of AF. On either side of F is a blackened region proportional to the divergence of the beam. To obtain smaller angle it is therefore necessary to decrease this opening by narrowing the slit in front of the monochromator; but it can be shown that for the same limiting angle greater beam openings may be used than with the double-slit set-up with no monochromator. This is why an intense beam can be obtained in spite of monochromatization; the lower limit of the angles for which diffraction may be observed is of the order of 20 min. The exposure time is of the order of 1 hour.

In neither set-up does the beam, determined by the slits, have a symmetry of revolution. To facilitate the interpretation of the results obtained, especially in the case of small angles, either the height of the beam must be reduced by means of horizontal slits so as to give a very narrow beam, or, on the contrary, the height of the slits must be increased, it being possible to consider the theoretical case of a planar beam of infinite height. The central diffraction spot then becomes a band whose blackness is a function only of the distance to the intersect of the direct beam.

The screen that intercepts the direct beam may well be constituted of a thin metal sheet, which allows enough of the direct beam to pass to impress the plate during the exposure; the image of the direct beam makes it possible to control the total quantity of X-rays received and to make a quantitative comparison of different negatives (for the CuKα ray, a copper sheet measuring 2/10 mm. in width would be suitable.)

The air that the direct beam meets between the sample and the film creates considerable scattering, for, in spite of the fact that X-ray diffraction by gases is slight, the diffracting domain is large and extends to the immediate vicinity of the film; it is therefore desirable to create a vacuum in this region.

Figure 4 gives a plan of the apparatus used by us; it is composed of the monochromator and the slits that determine the beam, placed on a platform attached to the tube, and of a vacuum-proof chamber containing the sample and the photographic film. This latter is formed by a tube closed at one end by an aluminum window (1/1000 mm.), through which the X-rays penetrate, and at the other by a cover ground conically carrying the film in a light-proof frame. This stopper also carries the evacuation pipe, and it is by rotating the cover that the apparatus is cut off from the pump. The sample is placed in air against the aluminum foil. It is in a small shallow tube with two very thin mica windows, into which the liquid may be poured or the powder may be pressed for examination. The apparatus is regulated as follows: The monochromator is first regulated in the manner described elsewhere;[2] by action of the slit A_1, the width of the beam, which should not exceed 20 to 30 min., may be determined; the edges of the slit A_2 are then brought to within a few hundredths of a millimeter of the outside edge of the beam. This setting is very accurate and cannot be

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observed simply through a fluorescent screen but must be controlled photographically. A plate is placed symmetrically to the slit with respect to the point of focus; on the same film the beam is photographed, first with the slit A_2 wide open and then with the same slit narrowed until its edges intercept the exterior edges of the beam. The relative position of the two superimposed images indicated by how much each edge of the slit should be opened. Once the beam is adjusted, the diffraction chamber is so placed that focussing occurs at the film; the metal sheet used as absorbing agent is then brought exactly on the beam by slowly rotating the chamber around a vertical axis passing through the sample. In this way the adjustment is made without disturbing the position of the sample with reference to the beam. The frame is then loaded, and the truncated cone is placed over the chamber. The apparatus is then evacuated. A blank negative must first be made without the sample in order to make certain that no fogging whatsoever remains on the film; only the path of the direct beam should appear, considerably reduced by the absorbing agent.

DIAGRAM INTERPRETATION

The problem is quantitative characterization of the extent of the central spot; the simplest procedure would be to measure the angle for which diffraction ceases, using formula (1). However, it so happens that in many cases this formula does not even give an approximate result. For a given negative, the size of the central scattering spot is quite easily defined, but the radius found in this way depends largely on the length of the exposure. Whereas, in characterizing a spectral ray, its width is measured at half intensity; this method cannot be applied here, as the center of the central diffraction curve is not experimentally accessible; it therefore becomes necessary to study the variation of the diffracted intensity with the angle. We wish to set forth the theoretical considerations that make it possible to use the relation between the experimental curve and the particle size.

These calculations have already been published,5/ and only the results will be given here. They are based upon the following hypotheses: The preparation consists of a group of particles all identical but which may have any given shape and orientation; they have a random distribution, and their density is low, that is, the relation of the total volume of the particles to the volume which is available to them is small (less than 10 percent). These particles may be in a vacuum or in a homogeneous medium; the central diffraction is conditioned by the electron density of the particle, that is, by the number of electrons per unit of volume; this is given by the formula

$$\Delta = \frac{NZ}{M};$$

where Z is the sum of the electrons in the atoms that form the molecule, M is the molecular mass, ρ the specific mass, and N Avogadro's number. Particles whose electronic density is Δ, suspended in a medium of density Δ', give the same diffraction pattern as particles situated in a vacuum

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having the same shape and a density of $\Delta - \Delta'$. It is therefore to a difference of electronic density that x-rays are sensitive; this first result is important. From a practical point of view, when studying a colloidal system, it is necessary to ascertain that the electronic densities of the micelles and of the solvent are not too close, otherwise the diffracted intensity will be extremely weak. Kratky has shown experimentally that cellulose solutions in different solvents give central spots that are similar, but whose intensity increases as the difference between the electronic densities of the micelles and the solvent becomes greater.

The amplitude of the wave diffracted by a particle is first calculated, and then the intensity diffracted in a given direction by the mass of the particles distributed at random. Let us consider a small element of the preparation which is thin enough to make absorption negligible and which contains N electrons grouped in particles composed of n electrons each; let $I_e^{(*)}$ be the intensity diffracted for small angles by an electron situated in the beam under consideration.

$^{(*)}I_e$ is given by Thomson equation:

$$I_e = \frac{I_0 e^4}{r^2 m^2 c^4} = 8 \cdot 10^{-26} \frac{I_0}{r^2}$$

I_0 is the energy transported by the incident beam, per cm^2 of section and per second, r is the distance from the sample to the film.

The diffracted intensity is given by the following equation:

$$I = N I_e n e^{-\frac{4\pi^2}{3\lambda^2} R^2 \varepsilon^2}$$

which equation is valid only when ε is sufficiently small to make the exponent small with respect to unity. R is the parameter which characterizes the particle size; it may be rigorously defined as follows: a coefficient equal to their atomic number is attributed to the center of the atoms of a given particle; if we consider the center of gravity of this group of points, R^2 is the mean of the square of the distances of each atom to its center, a coefficient equal to the atomic number of the atom being assigned to each square. It can be shown that R is none other than a dimension used in mechanics under the name of radius of gyration, that is, the length R such that the moment of inertia of the particle with respect to its center of gravity is mR^2, m being the total mass of the particle. R may therefore be calculated by a simple geometrical operation for a particle of given size and shape. For instance, a sphere of radius ρ has a radius of gyration

$$R = \sqrt{\frac{3}{5}}\ \rho = 0.77\rho ; \qquad (3)$$

for an ellipsoid of revolution with axes a, a, va,

$$R = \sqrt{\frac{2 + v^2}{5}}\ a. \qquad (3)$$

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The interest of formula (2) lies in the fact that it involves a single parameter, R, to characterize the size of the particle, but, conversely, the radius of gyration alone is obtained experimentally. Consequently, the geometrical dimensions of the particle can be deduced only if its form is known; if for instance we know that it is a sphere or an ellipsoid whose axes ratio is v, equations (3) give the spherical radius or the axes of the ellipsoid.

The diagram is elaborated in the following manner: The negative is passed through the microphotometer; if i is the galvanometric deviation for a given point on the negative and i_o the deviation corresponding to the unexposed partion of the film, the photographic density at this point is $\log \frac{i_o}{i}$. Now, for X-rays, and provided that the negatives are not too dark (density less than 0.7), the intensity received by the film per surface unit may be taken with a good approximation as proportional to the photographic density. This simple rule eliminates the standardization of the plate which is necessary for photometric measurements in the visible. Equation (2) may also be written:

$$\log I = \log N I_e n - \frac{4\pi^2}{3\lambda^2} (\log e) R^2 \varepsilon^2 \qquad (4)$$

We therefore construct not the curve (I, ε) but the curve $(\log I, \varepsilon^2)$. From (4) it is apparent that this curve must be a straight line, at least for the region of small angles ε; the angular coefficient α of this straight line gives the radius of gyration R

$$R = \sqrt{\frac{3}{4\pi^2 \log e}} \lambda \sqrt{\alpha}$$

For $\lambda = 1.54$ Å (CuKα), R is given in angstroms by the equation:

$$R = 0.416 \lambda \sqrt{\alpha} = 0.644 \sqrt{\alpha}.$$

The application of this formula implies that at a given point of the film, to be specific, for the small surface explored by the microphotometer slit, there exists a definite angle ε. In our set-up this condition is fulfilled only if we do not come too close to the direct beam, because of the beam's finite height. But, as we have already noted, by increasing the height of the beam we tend towards another limiting case for which calculations are possible: that of a beam with horizontal rays of great height. Calculation shows that save for a constant factor the intensity distribution in the central spot is given by the same equation (2). Formula (4) can therefore be applied without any change, and in this case the negative can be examined through a microphotometer slit of any given height.

The central diffraction produced by an albumen solution gives a good illustration of this method (fig. 5); it is apparent that the points of

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the curve ($\log I, \xi^2$), transposed from the curve I, ξ) form a straight line and from its slope the radius of gyration R = 23 Å is obtained. If we assume the albumen molecule to be spherical, we are led to a radius value ρ = 26.2 Å, that is a volume 74,000 Å^3, from which, taking the albumen density as 1.3, the molecular mass would be 58500; but this figure is too high, as compared with the values found for the molecular mass by other physical-chemical methods. To obtain a correct value of the molecular mass the molecule must be conceived as an elongated ellipsoid having an axes ratio of 2.4, and it so happens that this shape is a very probable one. Therefore, for the case where the volume of the particle is known beforehand, study of the central diffraction makes it possible to determine its shape.

From central diffraction data it is possible to draw information regarding the shape of the micelle; it must, however, be stated at once that for the general case where the micelles have a random orientation, this is difficult and rather inaccurate. The following two methods are theoretically possible.

1. Although the center of the central scattering curve masked by the direct beam cannot be reached experimentally, extrapolation of the straight part of curve (4) makes it possible to find the intersection of the curve with the axis of the ordinates, that is, to determine the value of $\log NI_e n$. Now, I_e, the intensity diffracted per electron, is known (Thomson's formula) if the intensity of the incident beam is measured; N, the total number of electrons, can be deduced from the mass of the sample that the incident beam encounters; this method therefore makes it possible to calculate n, the number of electrons contained in a particle, and consequently the volume of the particle; this value, in conjunction with the radius of gyration, gives an idea of the form of the particle - for instance the axes ratio if the particle is taken to be an ellipsoid of revolution. The necessary experimental measurement is no longer a study of how the diffracted intensity varies with the angle of diffraction, but a quantitative comparison of the intensity of the direct beam with the diffracted beam. A photometric method that makes the result possible has already been indicated.

2. Equation (2) holds only for small angles. If, instead of making any hypotheses touching the shape of the particles, attention is given only to elongated or flattened ellipsoids of revolution, accurate calculation of the curve (I, ξ) becomes possible for all values of ξ; from this we find that for ellipsoids of various shapes, but having the same radius of gyration, the curves of diffracted intensity which coincide in the central part follow different paths at the extremities in the region of large angles. Comparison of the experimental curve with the network of curves calculated for different values of the axes ratio of ellipsoids makes it possible to determine the shape of the particle; unfortunately it can be seen from figure 6 how small the deviation between the different calculated curves are. A good degree of accuracy cannot therefore be obtained by this method.

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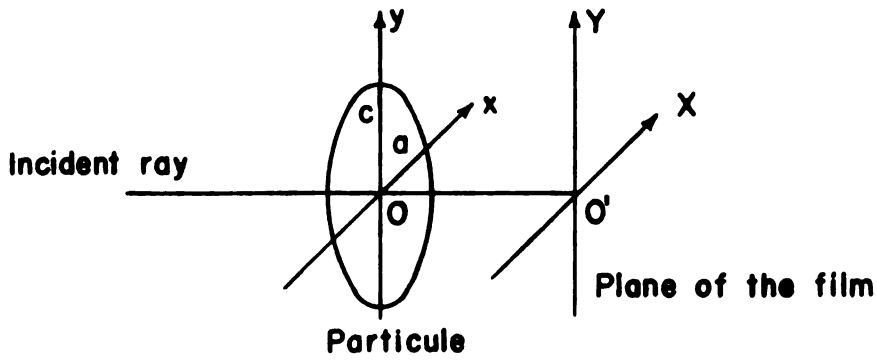

Fig. 7

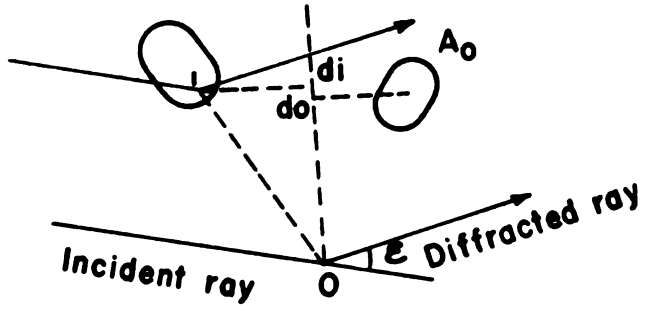

Fig. 8

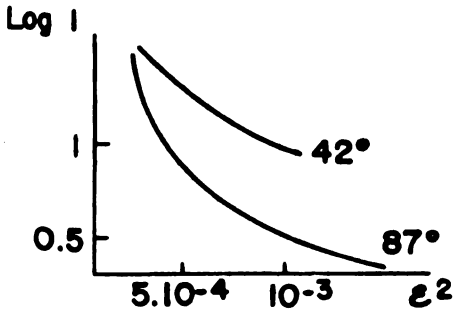

Fig. 10

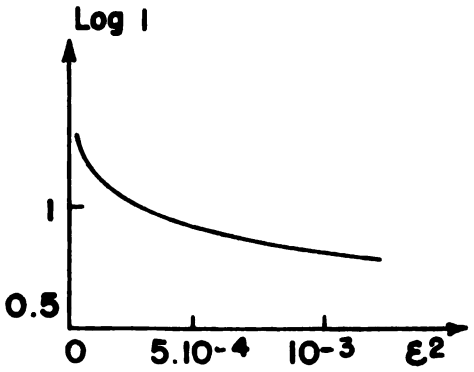

Fig. 11

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There is, however, a case for which the shape of the elementary particles is clearly evident: that is when the particles, instead of being directed at random, all have the same orientation. This case is important from a practical point of view, as such oriented preparations occur frequently. As examples we may mention fibrous substances, substances subjected to the action of certain fields, in motion, etc. Take, for instance, a group of ellipsoidal particles whose axes of revolution are all parallel and perpendicular to the X-ray beam; the central diffraction spot is no longer circular. The lines of equal blackness are ellipses similar in shape to the meridian ellipsis of the particle, but with a rotation of 90°, the diffraction extending farthest in the direction in which the particles are the narrowest. It is very suggestive, even if not strictly accurate, to say that X-rays give us an image of a particle whose dimensions are of the order of a few tenths of an ångstrom, and yet the apparatus that makes an enlargement of a million diameters possible is essentially a simple collimator. For the case of a group of oriented particles, the diffraction curve of the sample is identical with that of a single particle. Equation (2) takes the following form:

$$I = NI_e n e^{-\frac{4\pi^2}{\lambda^2} R_1^2 \xi^2} \qquad (5)$$

where R_1 has the following meaning: mR_1^2 represents the moment of inertia of the particle with respect to the plane passing through the center of the particle and perpendicular to the bissector of the incident and diffracted beams. For the case of an ellipsoid of axis Oy, whose meridian axes are c and a (fig. 7), the decrease in diffracted intensity is given respectively in the directions O'x and O'y in the plane of the film by the exponentials:

$$e^{-\frac{4\pi^2}{5\lambda^2} a^2 \xi^2} \text{ and } e^{-\frac{4\pi^2}{5\lambda^2} c^2 \xi^2}.$$

A and c may therefore be calculated directly; these are the equations used by Hosemann in his study on the fibers of cellulose and cellulose derivatives.

CASE OF SYSTEMS OF REAL PARTICLES

The theoretical considerations presented above are based on the identity of all particles and their random, loosely packed distribution. These conditions, however, are frequently not fulfilled. We will examine successively the effect of differences in the size of the particles and that of packing the particles more closely together.

A. Case of Hetero-dispersed Systems

Let us consider a group of particles of various different sizes, but which we assume to be distributed at random and at a sufficient distance from each other; each family of particles of a given size produces a

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diffraction governed by equation (2), and the total diffracted intensity is the sum of the functions corresponding to each family. This intensity can no longer be represented by an exponential, and in consequence the curve (log I, ξ^2) is no longer a straight line; it tends towards a straight line only when the angle ξ is small enough to bring us into the central part of the curve of the largest particle present. The slope of the curve decreases as the angle of diffraction increases, since the influence of the particles of small diameter is increasingly evident. Experimentally it can be shown that for the case of heterodispersed systems, convex curves directe upward are obtained. The limiting slope of the curve, as ξ tends toward 0, corresponds to a value of the radius of gyration close to that of the larges particles present.

Hosemann, in his study of cellulose, has tried to deduce the distribution of particles of different size experimentally; this is not possible directly by analysis of the curve. Starting with a group of given laws of distribution, the corresponding diffraction curves are calculated theoretically, and the curve is chosen that is closest to the experimental curve; but this partly arbitrary method, which gives only an indication, is nonetheless interesting in view of the complex nature of the problem to be solved. To sum up, central diffraction makes it possible (1) to determine if a system is hetero-dispersed, (2) to calculate the numerical value of the dimensions of the largest particles of the system, and (3) to estimate roughly the distribution of the different sizes of particles.

B. Particles in a Dense (Closely Packed) System

In the systems considered so far, where the particles at a distance from each other have a completely random distribution, the diffracted intensity is simply the sum of the intensities diffracted by each particle; but if the particles are drawn closer together, the waves diffracted by each particle may interfere, and the resulting intensity will be considerably modified. This is easy to see: Let us suppose that the particles are agglutinated in such a way as to leave no space between them. We than have a homogeneous system, and there is no longer any central diffraction.

Let us consider a system of identical particles: When they are brought into contact with each other, the system may be compared with a liquid, the particle acting as a liquid molecule. The calculation used to establish the theoretical diffraction curves of liquids[8] may be applied to the case of particles of uniform size. The following facts may thus be predicted: the diffracted central intensity decreases by interference and takes on the value

$$I\left(1 - \frac{\Omega}{V}\right) \qquad (6)$$

where I represents the diffracted intensity for the system in a state of low density, Ω the total value of the particles, and V the volume at their

8/ Compton and Allison, X-Rays and Electrons, MacMillan, New York, 2d edition, p. 177.

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disposal. If a value for the distance between the particle centers occurs frequently (equal to the diameter of these particles, as, for instance, in the case of spheres that touch each other) the diffraction curve presents a maximum for an angle whose value is about half that of the angle for which the intensity cancels out; thus, instead of a spot whose intensity decreases outward from the center, we find a ring; this case has actually been observed in the study of heterogeneous characters of solid solutions (fig. 14).

This, however, occurs only if the particle size is very regular; the general case, where the size varies and where the particles are also loosely packed, is obviously too complex to allow a theoretical study, as a mathematical definition of such a system is difficult. Kratky has treated a particular case (flat, parallel particles of varying thicknesses and in contact with one another). He found that the diffraction curve increases as the angle tends to that of zero diffraction. In first approximation one can say that for a system that is not too compact and is composed of irregular particles, the diffracted intensity decreases as a result of interferences between particles in the relation $1 - \frac{d'}{d}$), where d is the internal electronic density of the particle and d' the average electronic density of the system as a whole (the particles are considered to be in a vacuum), but the general aspect of the curve would not be greatly modified.

This result is justified by the following calculation: Given a system of K random particles, let d_1 be the projection of the distance from an electron i to an arbitrary center 0 situated on the bisector of the incident and diffracted rays that form the angle ξ. The difference in phase between the waves diffracted by the electron i and by an electron situated at 0 is $\frac{2\pi d_i \xi}{\lambda}$ (fig. 8). The intensity diffracted by the sample as a whole is

$$I = I_e \left[\sum_e e^{-\frac{2\pi i \xi}{\lambda} di} \right]^2 = I_e \sum_l \sum_m e^{\frac{2\pi i \xi}{\lambda} (d_l - d_m)}.$$

This sum can be divided into two parts:

1. If electrons l and m are in the same particle, the sum of the intensities diffracted by each of them is thus obtained, $\sum_k Ik$. This is the intensity I_{oo} diffracted when the particles are at a distance from one another.

2. The other terms correspond to electrons situated in different particles

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$$I/I_e = \sum_k I_k + \sum_l{}' \sum_m{}' e^{-\frac{2\pi i \varepsilon}{\lambda}(d_l - d_m)}, \qquad (7)$$

electrons l and m belonging to two different particles.

Let us calculate:

$$s = \sum_m{}' e^{-\frac{2\pi i \varepsilon}{\lambda}(d_l - d_m)}.$$

Let d_o be the projection of the distance from the origin to the center of the particle A_o to which electron l belongs; s can be written

$$s = \sum_m{}' e^{+\frac{2\pi i \varepsilon}{\lambda}(d_m - d_o)} e^{-\frac{2\pi i \varepsilon}{\lambda}(d_l - d_o)}$$

m may be in any particle except A_o.

Let us calculate a first summation σ_o for all electrons of particle A_o.

$$\sigma_o = \sum_m{}' e^{\frac{2\pi i \varepsilon}{\lambda}(d_m - d_o)} \sum_{(A_o)} e^{-\frac{2i\pi i \varepsilon}{\lambda}(d_l - d_o)}. \qquad (8)$$

The double summation of formula (7) is the summation of the σ corresponding to each particle. Therefore

$$I/I_e = \sum_k (I_k + \sigma_k);$$

the summation $\sum_m{}' e^{\frac{2\pi i \varepsilon}{\lambda}(d_m - d_o)}$ extends to all electrons belonging to particles other than A_o, that is, to all the space surrounding particle A_o. Let us suppose A_o to be composed of electrons whose density equals the average density d' of the electrons in the sample as a whole and let the summation $\sum_m{}'$ extend to these electrons. The hole due to particle A_o is thus suppressed and, because of the irregular distribution of the particles, summation $\sum'$ extends to a cubic space that is statistically homogeneous. Consequently, it must have a very low value. Hence,

$$\sum_m{}' e^{\frac{2\pi i \varepsilon}{\lambda}(d_m - d_o)} + \sum_{(A_o)}{}' e^{\frac{2\pi i \varepsilon}{\lambda}(d - d_o)} \neq 0 \qquad (9)$$

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$\sum'(A_o)$ extends to the electrons that would occupy particle (A_o) at a density d'. Let d be the true electron density of particle A_o; summations $\sum'(A_o)$ and $\sum(A_o)$ of formula (3) apply to the same volume, but filled with electrons of different electronic densities. Therefore

$$\sum'_{(A_o)} = \sum^{*}_{(A_o)} \cdot \frac{d'}{d},$$

But the intensity diffracted by A_o is:

$$I_o/I_e = \left[\sum_{A_o}\right]^2 = \sum_{(A_o)} \sum^{*}_{(A_o)}$$

From (9), therefore,

$$\sigma_o = - \sum^{*}_{(A_o)} \frac{d'}{d} \cdot \sum_{(A_o)} = - I_o \frac{d'}{d}.$$

In the same way, for each particle:

$$\sigma_k = - I_k \frac{d'}{d},$$

From which it is apparent that

$$I/I_e = \sum_k I_k \left(1 - \frac{d'}{d}\right) = I_\infty \left(1 - \frac{d'}{d}\right).$$

Although this calculation presents rather rough approximations (formula (9)), the result is interesting in that it justifies the application of the method established theoretically for very widespread systems to more compact ones, which in actual practice occur very frequently. It is, however, obviously valid only when the apparent density d' is not too close to d, because for too closely packed systems, the particles in contact no longer have random shape but are deformed in such a way as to eliminate interstitial spaces. As a system becomes more and more compact it may be considered as a homogeneous body pierced by a certain number of cavities; it is then the cavities that are few and irregularly distributed. Now, an optical theorem that applies equally in the case of X-rays shows that the diffraction pattern of such a body is the same as that of the complementary object where only the cavities are filled with substance. In this case, the theory of dispersed systems applies rigorously, but the values obtained thus give the dimensions of the holes.

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To sum up, the following results have been obtained theoretically:

1. With the present experimental set-ups, particles, in order to be perceived by central diffusion, must measure between 10 and 500 Å; for larger particles, the radius of the central spot is too small to be observed; for smaller particles, the spot is too extended and its intensity too weak.

2. For homo-dispersed systems of low density, the experimental curve can be used to obtain an accurate value characteristic of the particle size, its radius of gyration.

3. For hetero-dispersed systems, but in which particles are not too closely packed, an idea of the distribution of particle sizes may be obtained. If the system is both compact and hetero-dispersed, no accurate quantitative results can be obtained experimentally.

4. If the particles have a common orientation, it is possible to find their shape. If, on the contrary, the orientation is random, this becomes difficult unless their volume is known beforehand.

COMPARISON WITH MEASUREMENT OF THE WIDTH OF THE LINES IN DEBYE-SHERER DIAGRAMS

When X-rays were first used in crystal analysis, Sherer indicated a method for determining the size of fine crystal particles; when a powder is composed of very small crystals, the rings of a Debye-Sherer diagram become hazier as the crystals become more minute. A number of authors have studied the theoretical relation between the width of the lines and the size of the elementary crystallites, a relation that has been used in experimental work. Now the direction of the incident beam is a direction along which the waves diffracted by all the atoms of the crystal are in phase; as in the case of selective reflection we may call this the reflection of index 000. The central diffraction spot, then, appears as an enlargement of this spot of diffraction 000, and for a crystallized body, the study of central diffraction would be a special case of the study of the width of the lines. But one of the advantages of our method is immediately apparent. The central diffraction spot is much more intense than the D.-S. rings. The intensity diffracted by all the crystallites of the sample adds to it, whereas only a negligible number of them are directed in such a way as to diffract the incident rays at a given point in a D.-S. ring. In actual fact, the two methods are not as comparable as it seems at first glance and may lead to different results. The theoretical study of the width of D.-S. lines is based upon the hypothesis that every grain is a perfect monocrystal; it is therefore only in cases where each grain is a monocrystal that the two methods give identical results. In general, central diffusion leads to a larger particle size, when several small crystals are united in a single grain of isolated matter. Moreover, there may be other causes for the widening of D.-S. lines, as, for instance, certain crystal perturbations or variations in lattice from one crystal to another; but the observed widening of the lines is attributed solely to the particle

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size. It is therefore to be feared that the calculated dimensions will be too large. If now we take up amorphous bodies, where the relationships of the atoms in contact are rather vague and fluctuating, the D.-S. lines are replaced by very wide rings; but these rings are the same whether the body is compact or finely divided (vitrous silica the solution of colloidal silica). For instance, amorphous carbon gives a ring having the same average diameter as the principal line of crystallized graphite; the width of this ring gives us the size of the region in which the carbon atoms have the relative distribution of the atoms in the graphite crystal, but it gives no indication of the size of the grain of powdered carbon. On the contrary, the central diffraction spot is characteristic of the state of division of matter; it is completely independent of the internal structure of the grains. This is what gives the method its generalized character; it applies equally to amorphous and crystal bodies. The grain that it sets in evidence has a physical individuality, whereas widening of the D.-S. lines, which can be applied only in the case of crystal bodies, gives the dimensions of a region having crystallographic individuality.

APPLICATIONS OF THE METHOD

We shall now review the applications of this method that have already been effected. In many instances we are dealing only with partial or preliminary work that has in no wise exhausted the subject and that will have to be taken up again with the help of other physical-chemical methods.

1. Large Molecules

Theoretical work has shown that the most accurate results are obtained for homo-dispersed substances having low particle density. From this it would appear that one of the most interesting fields of application should be the study of large molecules with a molecular weight of 10,000 to 100,000, there being chemical reasons for thinking that all micelles are identical. We have run only one preliminary experiment on albumen, and Kratky[9] recently studied chrymotrypsine. It is to be predicted that systematic studies in conjunction with other methods for determining high molecular weights should give very worthwhile results.

2. High Polymers

The study of micelles formed by molecular polymerization has given rise to several papers. In collaboration with M. J. Devaux, we have studied the polymers of methyl methylacrylate (plexiglas) in the solid state. This body produces no central diffusion whatsoever, whereas its acetone solutions give central-spot diagrams. Moreover, the diffraction diagrams of these solutions show the same rings as that of solid plexiglas (fig. 9); the inner structure of the solid body, therefore, is the same as that of the micelles. It seems likely that these micelles already have their individual character in the solid state, but that they are so closely packed that all heterogenity disappears. Solution liberates the micelles, but it is also possible that the solvent has a more rigorous action and that the polymerized chains are more or less broken up. However

9/ Kratky, Naturwissenschaften, 31 (1943), p. 46.

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this may be, X-ray study has established the following facts: Different solutions of samples prepared under similar conditions give very similar central diffusion curves. The state of dispersion of a given polymer is thus rather well-defined; the graphs ($\log I, \xi^2$) are always smooth curves; the system is therefore hetero-dispersed.

Assuming that solution does not cause a break in the chains, this result shows that chain lengths would vary greatly for a given state of polymerization. We have made a study of the variation of these scattering curves with that of the polymerization temperature; the conclusion reached is that for all these hetero-dispersed systems nothing can be said about the largest particles - particles whose dimensions exceed 400 Å are too large to be accessible to our present experimental set-up; however, for small particles one finds that the higher the temperature of polymerization, the fewer the number of small particles. This is shown by the two curves (fig. 10) obtained with samples of plexiglas polymerized at 46° and 87°, respectively. The slope of curve (87°) is steeper than that of curve (46°) It is interesting to compare this fact with the other physical properties of different plexiglas samples, only a certain number of which show variations.[10] Lastly, plexiglas containing a plasticizer (butyl phthalate) gives a central diffusion spot in the solid state; this shows that penetration of the plasticizer between the micelles brings about a heterogeneous condition; ordinary diagrams show the unchanged rings of pure plexiglas on the one hand and of the plasticizer on the other. The curve ($\log I, \xi^2$) is composed of two distinct parts (fig. 11); it may be interpreted by saying that small particles of plasticizer exist side by side with large plexiglas molecules; in view of the very compact volume of this mixture, quantitative measurements would be subject to doubt.

The experimental work of Hosemann[3] and Kratky[4] has also been on high polymers, in particular cellulose and its derivatives. Using oriented preparations of cellulose, Hosemann has determined the shape and size of the micelles. They are hetero-dispersed systems in which he has attempted to study the distribution of particles of different sizes.

3. Bodies Having a Granulated Structure

In this category are included substances in which the particle has no chemical but only a physical individuality. We may expect, therefore, that the size of many of the grains will vary considerably and that such bodies will have rather high densities in the solid state - that is to say, that the grains will be close together. The conditions are therefore quite different from those assumed in our theoretical calculations, but the practical interest of study by X-ray is great, even though it gives only qualitative results, because of the difficulty encountered in characterizing the size of these submicroscopic particles by other methods. The electron microscope alone has sufficient power of resolution to show up such grains. An important example is found in the study of catalysts whose activity is proportional to the total surface - that is, to the fineness of the elementary grains. We have, for instance, verified the fact that catalytic Raney nickel, which is more active than ordinary reduced nickel, has a much

10/ Boutry, Revue d'Optique, 20 (1941), p. 1.

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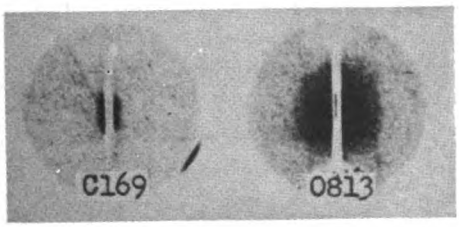
Plate 2



a b

Figure 12

a) unactivated carbon.
b) activated carbon. Reproduced in full size.

Distance from sample to film: 82 mm.
CuK_α radiation.
Exposure: 30 minutes.

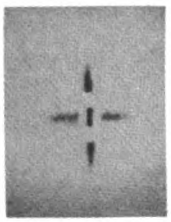
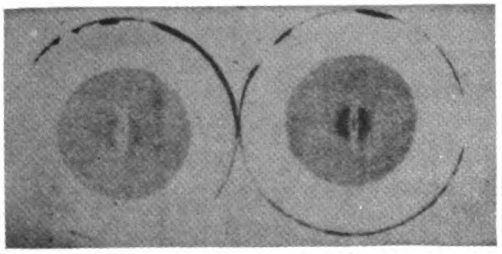


Figure 13

Scattering at center of an AlCu alloy crystal (5% Cu, tempered from 450°, then hardened for 4 hours at 100°). The incident X-rays are parallel to one edge of the cube of the crystal. Each trace corresponds to a plane of copper atoms parallel to a face of the cube.

Distance from sample to film: 37 mm. MoK_α radiation.



a b

Figure 14

Central scattering for a sample of Al-Zn alloy (34% Zn).
a) immediately after tempering.
b) after 4 days at room temperature (same conditions as Figure 12).

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finer granular structure. It is evident that applications of practical interest may already be foreseen.

In collaboration with Brusset and Devaux, a preliminary study of various carbons has been made, the first results of which we have published elsewhere;[11] we were able to show in particular that activated carbon gives very extensive central diffusion, whereas the same sample before activation gave only a very limited spot (fig. 12). This diffusion probably is caused not by the presence of small particles whose formation would be difficult to explain, but rather by small cavities which the activation treatment would have emptied of their contents.

4. Another field of application is the determination of heterogeneous characters in a solid body. The sample is no longer formed by material grains separated from one another, but by a continuous solid in which regions of small dimensions have a different composition from the average. We have examined the case of solid supersaturated metallic solutions during decomposition. The initial state is that of a solution of homogeneous substitution with a regular distribution of the different atoms; following thermal treatment, the atoms of the dissolved metal group themselves in nuclei of small dimensions. These solutions evolve towards a stable state, in which two phases having distinct crystalline structures coexist. The central diffusion of X-rays makes possible an accurate study of the intermediate states, which have great technical importance owing to the mechanical properties that certain alloys may thus acquire. We can do no more than mention here the results that have been developed in previous papers.[5/12/13] In the case of Al-Cu and Cu-Be alloys, the atoms form masses whose distribution is determined by the orientation of the alloy crystal; in a noncrystalline sample, where all these masses have a common orientation, the central diffusion spot assumes a characteristic shape from which the shape of the atom masses may be deduced (fig. 13). It can thus be shown that the dissolved atoms are grouped in flat nuclei parallel to the faces of the crystal cube, and the growth of their dimensions, diameter, and thickness may be observed as a function of thermal treatment. In other instances (Al-Ag and Al-Zn alloys), the masses of atoms have no well-defined form, for the appearance of the central diffusion spot does not depend on the orientation of the alloy crystal and always has a circular symmetry, but in this case the central scattering spot is formed by a ring (fig. 14). We have already indicated that this ring is a sign that the masses nearest to each other are placed at a distance that remains fairly close to a given value. It would appear, therefore, that in the regions where the dissolved atoms concentrate, a kind of periodic precipitation occurs.

This brief review of a few applications of the method of central scattering shows in the study of how many different problems it can be used, and it is our aim in this paper to draw the attention of chemists and physical chemists to this new physical method; its application does not present serious experimental difficulties, and it is only in their hands that, in conjunction with other physical-chemical methods, this new technique can fulfill what it seem to promise.

11/ Brusset, Devaux. Guinier, Comptes rendus, vol. 216, 1943, p. 152.
12/ Guinier, Jour. Phys., vol. 3, 1942, p. 124.
13/ Guinier, Comptes rendus, séance du 17 mai 1943.

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